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Short communication

Highly efficient, recyclable and alternative method of synthesizing phenols from phenylboronic acids using non-endangered metal: Samarium oxide

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ABSTRACT

Oxidation of phenylboronic acid to phenol is one of the important industrial processes and it is generally employed in the plastic, explosive and drug manufacturing industries. Over the past decades, numerous efficient methods have been described for the generation of phenols from phenylboronic acids in the presence of oxidant. However, these methods suffered from various limitations, including the use of expensive, toxic reagents and sophisticated protocol to synthesise the phenols. Additionally, some of these reported literatures employed endangered metals, in which mankind is facing the risk of limited supply of these elements in 20 years' time from now. As such, a viable alternative and green method for achieving organic synthesis is highly sought after by the chemists of today. Herein, we report for the first time a facile, efficient and alternative method in the preparation of phenols from phenylboronic acids using non-endangered metal as catalyst. In all cases, all phenols were afforded in satisfactory yields (81–96%) by employing column-free method. In the recyclability study, the Sm_2O_3 catalyst was found to possess good catalytic performance, even after being reused for five consecutive times (96–91%). In addition, SEM result revealed that the morphology of the recycled Sm_2O_3 catalyst was well preserved after five successive uses, which indicate no observable changes occurred in the recovered catalysts. As a final note, the current method is anticipated to be useful for industries manufacturing chemical intermediates as it provides an alternative method of catalysis by using a non-endangered metal in organic transformations.

1. Introduction

Oxidation reaction is considered as one of the most fundamental reactions in chemistry [1–3]. In particular, the oxidation of cumene and decomposition of cumene peroxide to yield phenol, is one of the common strategies in the industrial preparation of phenol and acetone [4]. In the chemical industry, phenols are widely used as the starting materials in the manufacturing of pharmaceuticals, polymers, natural products and agrochemicals [5,6]. Unfortunately, the cumene process is a multistep process and encompasses the use of high temperature to obtain the phenol. This process has also several other drawbacks such as low yield and high operational cost [2,4]. Furthermore, it is known that oxidation process is commonly unstable and this may lead to the production of environmentally harmful by-products. As such, a viable alternative route to phenols synthesis is urgently needed, especially if it involves a green oxidation process that is efficient and eco-friendly is highly sought after among the scientists and industrial players alike.

Over the years, enormous literatures were generated based on the use of the phenylboronic acids to produce phenols. These methods were capable to facilitate efficient oxidation of phenylboronic acids to synthesize phenols, while producing fewer toxic by-products into the environment [5–7]. Additionally, the use of hydrogen peroxide (H_2O_2) as oxidant offers various benefits, which includes low cost, high oxygen content, eco-benign and safer method of oxidation [8–11]. However, most of these methods require the utilization of suitable catalysts. In some cases, the utilization of transition metals and unsustainable methods for facilitating the oxidation of phenylboronic acids to phenols were also reported [6,12–15].

According to a survey, the technological development in industries are not neutral in the use of all elements. Certain metals such as

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palladium, copper, nickel and gold are favoured, contributing to their fast depletion known as resource deficits. Considering the ill-effect contributed by the unsustainable use of elements on our environment, society and the economy, scientists have put forth a vital move to protect these "endangered elements". Elemental Sustainability is a philosophy that is coined to protect these endangered elements, and at the same time, encourage the balance use of elements in periodic table to achieve industrial development and sustainable synthesis [16].

As part of our continuous effort in the search for efficient and sustainable catalyst for organic transformations, herein, we would like to demonstrate the use of samarium oxide (Sm_2O_3) as an alternative method in achieving sustainable production of phenols via phenylboronic acids in the presence of H_2O_2 (Fig. 1). Lately, the use of lanthanide metals has gained much attention among scientists due to its unique electron configuration, robustness and high catalytic activity of surface structure in catalysing chemical processes [17]. One such example is the recently developed samarium nanoparticles as sustainable catalysts in Pechmann and coupling reactions [18,19]. To date, our group is the first to report on the utilisation samarium oxide to produce phenols. The current method is of significant and useful in the chemical industry for manufacturing chemical intermediates as it encompasses the use of non-endangered metal for organic transformation.

2. Experimental

2.1. Chemicals and instrument

All chemicals and solvents utilized in this study were purchased from Sigma-Aldrich Malaysia. They were used without purification unless stated. The phase formation and nanostructure of Sm_2O_3 were performed using an X-ray diffractometer (X'Pert Pro PW3040 MDP/Panalytical) with Cu-Kα radiation source and a scanning electron microscope (JEOL JSM-6360LA). The X-ray diffraction (XRD) pattern was collected within 20–80° in with increment step size of 0.033°. In addition, a Bruker Nuclear Magnetic Resonance (NMR) spectrometer was employed to analyze samples and all the spectra were recorded on proton (^{1}H) (400 MHz) and carbon-13 (^{13}C) (100 MHz). All chemical shifts (δ) were quoted in the NMR as parts per million (ppm). The molecular mass of the samples was analyzed over the Shimadzu QP2010SE Gas Chromatography Mass Spectrometry (GC–MS). The values of all molecular mass were recorded in spectra as unit of mass over charge ratio (m/z).

2.2. Synthesis of Sm_2O_3 catalyst

The Sm_2O_3 nanoparticles were synthesized via hydrothermal method starting from 99.9% $Sm(NO_3)_3{\cdot}6H_2O$. A $Sm(NO_3)_3$ solution was prepared and mixed with oleic acid (OA) and *tert*-butylamine (TA) in a fixed ratio of 1:1:1 for Sm:OA:TA. The clear homogeneous solution was adjusted to pH 12 with NaOH. The mixture was transferred into a Teflon lined stainless steel autoclave and heated at 200 °C for 72 h in an oven. The obtained precipitate was washed with ethanol for several times before calcination at 750 °C in a furnace to obtain the Sm_2O_3 nanoparticles.

2.3. General method for phenols synthesis

Phenylboronic acid was added to a round bottom flask suspended with hydrogen peroxide 30% wt/v (3 mL) as oxidant, and samarium oxide (10 mmol) as catalyst. The mixture was then heated at about 80 °C for 4 h. Product formation was monitored by using thin layer chromatography (TLC). The reaction mixture was left to cool at room temperature and the catalyst was separated from the reaction mixture by filtration. Subsequently, the organic layer was separated, washed with sodium bicarbonate solution and the resulting aqueous layer was washed three times with ethyl acetate (3 × 10 mL). The combined organic layers were concentrated under reduced pressure to obtain the dried crude product. Lastly, the single pure product was afforded by using the precipitation method. The recycled samarium oxide was employed to synthesize different phenols under the same condition.

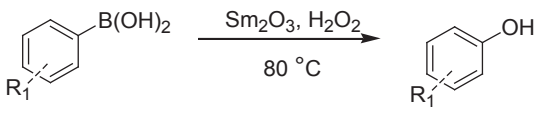


Fig. 1. Conversion of phenylboronic acids to phenols using samarium oxide as catalyst and hydrogen peroxide as oxidant.

3. Results and discussion

The Sm_2O_3 catalyst were characterized by XRD and SEM analyses as shown in Fig. 2. The synthesized precipitates transformed from amorphous intermediate phase to crystalline Sm_2O_3 phase when calcined at 750 °C. The Sm_2O_3 phase was found to be cubic single phase without any presence of secondary phase (Fig. S1). This highly crystalline Sm_2O_3 phase matched with Inorganic Crystal Structure Database (ICSD) 98-001-2948. Based on the SEM image (Fig. S2), it can be observed that most of the particles are spherical with a size distribution between 120 and 300 nm. In order to investigate the uniformity of element distribution in Sm_2O_3, EDX mapping was carried out. The inset of Figure S2 show the elemental mapping of O and Sm, demonstrating homogeneous distribution of Sm_2O_3 with high purity. FTIR spectrum as shown in Fig. S3 indicated that the stretching vibrations of Sm^{3+}–O are located at 877 cm^{-1}, 522 cm^{-1} and 439 cm^{-1}, respectively. The strong band at 1427 cm^{-1} was ascribed to the Sm-O-Sm deformation vibration whereas the weak band at 3788 cm^{-1}, 2323 cm^{-1} and 2968 cm^{-1} corresponded to the stretching and bending vibrations of –OH. These weak –OH bands were observed due to the marginal presence of water within the Sm_2O_3 nanoparticles.

In the optimisation study of reaction condition, a round bottom flask (50 mL) were equipped with phenylboronic acid (1 mmol) as the model substrate, hydrogen peroxide 30% (3 mL) as oxidant and Sm_2O_3 (10 mmol) as catalyst. The reaction mixture was subject to heating at 60 °C for about 1 h. The formation of **3a** was monitored using TLC analysis. At this stage, about 54% reaction's yield was observed for **3a** after 1 h (Table 1, entry 1). Increasing the reaction temperature has also increased the yield of 3a (Table 1, entry 3). Furthermore, it was observed that amount of Sm_2O_3 used could also affect the catalytic performance on **3a** synthesis. The increased amount of Sm_2O_3 has resulted a better yield of **3a** with 10 mmol Sm_2O_3 as the optimum amount of catalyst in **3a** synthesis (Table 1, entry 7. In addition, different amounts of hydrogen peroxide used also have an effect on the yield of **3a** formation. Laboratory result showed that 3 mL of H_2O_2 gave the best result in the formation of **3a** (96%), when employed for the oxidation of

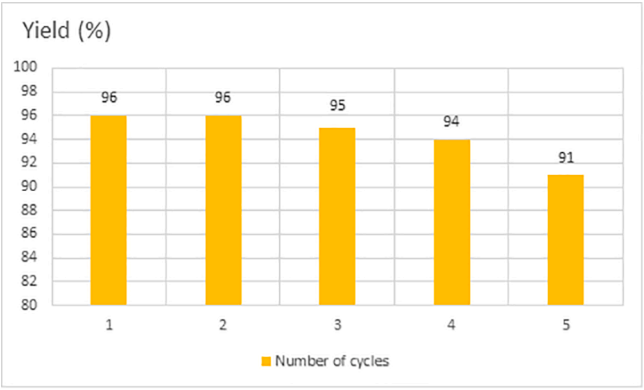


Fig. 2. Recyclability experiment using **3a** as a model product.

Table 1
The optimization experiment conducted by using phenylboronic acid to synthesize **3a.**

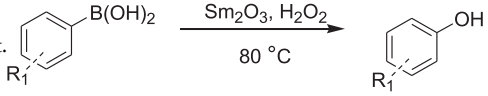
Entry	H_2O_2 (mL)	Sm_2O_3 (mmol)	Time (h)	Temperature (°C)	Yield[a] (%)
1	3.0	10	1	60	54
2	3.0	10	1	70	67
3	3.0	10	1	80	79
4	3.0	10	2	90	78
5	3.0	–	1	80	–
6	3.0	5	1	80	83
7	3.0	10	1	80	90
8	3.0	15	1	80	89
9	–	10	1	80	–
10	1.0	10	1	80	91
11	2.0	10	1	80	93
12	3.0	10	1	80	96

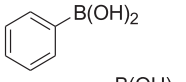
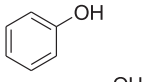
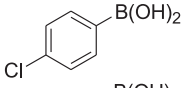
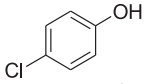
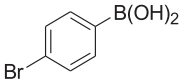
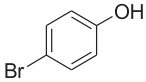
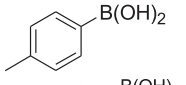
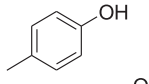
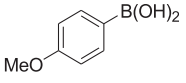
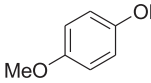
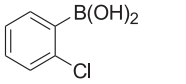
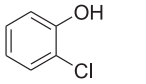
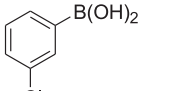
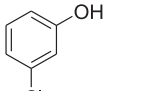
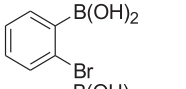
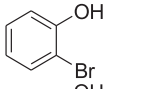
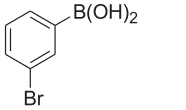
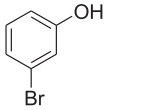
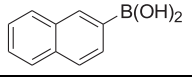
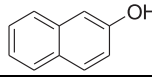
[a] Isolated yield of product **3a.**

phenylboronic acid (Table 1, Entry 12). On the contrary, when Sm_2O_3 was used alone in the absence of H_2O_2, **3a** was not formed and it was quite clear that the H_2O_2 acted as oxidant in this reaction (Table 1, entry 9). Based on all the results on hand, it was determined that 3 mL of H_2O_2 and 10 mmol of Sm_2O_3 (Table 1, entry 12) were suffice to promote oxidation of phenylboronic acid into phenol with excellent yield.

To widen the scope of our study, the optimized condition was applied to synthesize different phenols, using different phenylboronic acids bearing with the electron-withdrawing and donating groups as substrates (**3a-j**). In all cases, all phenols were afforded in satisfying yields (Table 2, entries 2–10) by using Sm_2O_3 as catalyst. Interestingly, napthol was also able to be synthesized from the same procedure by using a fused ring system, and the yield of the corresponding product was found to be in 90% (Table 2, entry 10). In this work, the hydrogen peroxide was chosen as the oxidant in the conversion of phenylboronic acids to phenol due to the simplicity and clean profile of hydrogen peroxide [29]. Furthermore, it is also noteworthy to report that the phenols produced from this work was afforded via the precipitation method. All synthesised phenols were characterized via the NMR and GC–MS experiments. Overall, the current protocol was considered as more superior than previous reported methods [20–28], as it uses a non-endangered metal, solvent-free method and non-sophisticated protocol in the synthesis of phenols (**3a-j**).

Table 2
Formation of phenols from phenylboronic acids with the aid of Sm_2O_3 as catalyst.



Entry	Compound	Substrate	Product	Yield[a] (%)
1	3a			96
2	3b			94
3	3c			95
4	3d			92
5	3e			93
6	3f			86
7	3g			85
8	3h			81
9	3i			83
10	3j			90

Next the reusability of the Sm_2O_3 catalyst was investigated after separation from the crude reaction. In the recyclability test, our laboratory result showed that the Sm_2O_3 catalyst is not only recoverable, but also catalytically active even after reused for five consecutive times. As illustrated in Fig. 2, the catalytic activity of the Sm_2O_3 was mostly retained, with the desired products afforded in excellent yields (91–96%) after five consecutive runs. In addition, the SEM result (Fig. S4) revealed that the morphology of the recycled Sm_2O_3 catalyst was well preserved which is comparable to Fig. S2 This indicates that there were no observable changes occurred in the recovered catalyst after five successive uses. Based on these results, the current protocol fits the green requirement, since the current protocol promotes the use of sustainable catalyst and the catalyst is catalytically active and reusable as shown in the recyclability experiment [30–34].

Last but not least, the merit of this work was analyzed by comparing the catalytic performance of current work to previous literatures in the synthesis of phenol (**3a**). Based on Table 3, it was found that the catalytic performance of current method is comparable to previous methods, judging from **3a** synthetic yield. Moreover, most of these reported methods adopted the use of endangered metals as catalysts, toxic reagents and tedious protocol in the preparation of phenols from phenylboronic acids. The use of non-endangered metal as catalyst is significant for promoting a more sustainable and greener organic transformations. This environmental-friendly catalyst holds promising potential in both the chemical industry and academia in accomplishing organic processes.

4. Conclusion

In this work, a facile, efficient and the use of non-endangered metal for synthesizing phenols from phenylboronic acids is reported. Various benefits resulting from the use of Sm_2O_3 as catalyst have been identified,

Table 3
Analysis of the merits of current protocol in the synthesis of **3a** by comparing its yield to previous literature.

Entry	Catalyst	Time (hour)	Yield (%)	Reference
1	Sm_2O_3/ H_2O_2	1	96	Current work
2	Copper nanoparticle biohybrid	6	90	[20]
3	C70 fullerene/Photocatalyst/O_2/ $CHCl_3$	12	99	[21]
4	Graphitic carbon nitride/Blue LED	6	95	[22]
5	Pd/Bentonite nanocomposite/H_2O_2	0.25	94	[23]
6	2,2-Methoxy-2-phenylacetophenone/DIPEA/light bulb irradiation	72	76	[24]
7	Pd/KB Polymeric nanocomposite	0.08	95	[25]
8	*tert*-Butyl hydrgen peroxide/ Potassium *tert*-Butoxide.	5	92	[26]
9	Sodium sulphite/oxygen in air	1	100	[27]
10	Silica chloride/ H_2O_2/Acetonitrile	0.08	100	[28]

including a phenol synthetic protocol that utilises benign and inexpensive catalyst, as well as free of endangered metal, but at the same time able to produce phenols in excellent yields (81–96%). In the recyclability study, the Sm_2O_3 catalyst was found to possess good catalytic performance, even after reused for five consecutive times (91%). Moreover, all phenols were afforded by employing the column-free method. The current protocol fits the green requirement, since the current protocol promotes the use of sustainable catalyst and the catalyst is catalytically active and reusable as shown in the recyclability experiment. As a final note, the current method is anticipated to be useful in the industry in the foreseeable future for manufacturing of chemical intermediates and provide an alternative method of catalysis, for it avoids the use of endangered metals in organic transformations.

CRediT authorship contribution statement

Hanis Mohd Yusoff: Conceptualization, Methodology, Investigation, Data curation, Writing - original draft. **Prasana Devi Bala Chandran:** Conceptualization, Methodology, Investigation. **Fatin Amira Binti Sayuti:** Conceptualization, Methodology, Investigation. **Su-Yin Kan:** Conceptualization, Methodology, Investigation. **Siti Aisha Mohd Radzi:** Data curation, Writing - original draft. **Fu-Siong Julius Yong:** Data curation, Writing - original draft. **Oon Jew Lee:** Conceptualization, Methodology, Investigation, Data curation, Writing - original draft. **Poh Wai Chia:** Conceptualization, Methodology, Investigation, Data curation, Writing - original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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